A method for direct observation of quantum tunneling in a single molecule.

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An application of impedance measurement technique (IMT) for a detection of quantum tunneling in molecular structures is investigated. A charged particle which tunnels in a two-well potential is electrically coupled to a high-quality superconducting LC-circuit(tank) that makes possible a measurement of the electric susceptibility of the molecule at the resonant frequency of the tank. The real part of this susceptibility bears information about the tunneling rate through a measurable parameter - a phase angle between the tank voltage and a bias current applied to the tank. It is shown that the present approach is highly sensitive and allows the monitoring of the tunnel motion of charged nuclei in a single molecule.

Tunneling of a particle between minima of a double-well potential represents a pure quantum phenomenon which takes place in many physical and chemical systems[1,2]. Splittings of molecular energy levels due to tunneling motion of constituent nuclei have been observed using spectroscopical methods[3,4,5] as well as methods of nuclear magnetic resonance relaxometry[6]. The measurements have been performed with samples containing a large number of molecules. Recent progress in molecular manipulation with a scanning tunneling microscope tip[7,8] makes possible a creation of single-molecule devices, and, in particular, apparatuses which use tunneling effects[9].

Here we propose to employ an impedance measurement technique[10,11] for contactless characterization of quantum tunneling in single molecules. This technique has provided a simple and reliable method for experimental investigation of tunneling in magnetic systems, especially, in superconducting flux qubits[12,13,14]. In the framework of IMT method the qubit's loop is inductively coupled to a high-quality LC circuit (tank) driven by a time-dependent bias current. An interaction of the tank with the qubit modifies an effective inductance of the tank and produces a shift of its resonant frequency. As a result, a voltage in the LC-circuit, $\langle V_T(t)\rangle = V_T\cos(\omega t + \Theta)$, has been displaced in phase from the bias current, $I_{bias}(t) = I_{ac}\cos\omega t$, by the angle Θ. A dependence of the angle Θ on the bias applied to the qubit has demonstrated IMT dips which are indicative of quantum tunneling in the qubit. A tunneling rate between wells is determined by the width of the dips. From the theoretical point of view the tangent of the difference between phases of voltage and current, $\tan\Theta$, is proportional to the real part of a magnetic susceptibility of the qubit.

To study intra-molecular tunneling of a charged particle, say, a proton or another light nucleus, in a two-well potential $U(z)$, we have to measure an electric susceptibility of such a molecule. To do this, the molecule is placed between plates of the tank's capacitor C_T, so that the charged particle tunnels along lines of the intra-capacitor electric field $E_z = V_T/d$. Here V_T is a voltage applied to capacitor's plates which are separated by the distance d. We assume that the two-well potential $U(z)$ has minima at $z = \pm z_0$. Taking into account the lowest tunneling doublet of energy eigenstates we describe quantum dynamics of the system by the Hamiltonian

$$H = \frac{\Delta}{2}\sigma_x + \frac{\varepsilon}{2}\sigma_z - (\lambda V_T + Q_0 + f)\sigma_z + H_T. \tag{1}$$

Here Δ is a rate related to the particle's tunneling between the wells, ε is a bias describing an asymmetry of the wells. This bias can be changed by applying an additional constant voltage to the capacitor C_T. A position of the particle is characterized by the Pauli matrix $\sigma_z : \hat{z} = z_0\sigma_z$, so that an interaction with the intra-capacitor electric field E_z is given by the term $-\lambda V_T\sigma_z$, where $\lambda = e(z_0/d)$. We add a qubit's internal heat bath with a variable Q_0 and an auxiliary external force f. It should be noted that thermal fluctuations of the tank voltage contribute to decoherence and relaxation of the qubit together with internal mechanisms. We consider the tank, having a resonant frequency $\omega_T = 1/\sqrt{L_T C_T}$, as a quantum harmonic oscillator with the Hamiltonian ($\hbar = 1$):

$$H_T = \omega_T(a^+a + 1/2) - (a + a^+)Q_b - L_T\hat{I}_T I_{bias} + H_{TB}. \tag{2}$$

The tank's excitations are described by creation/annihilation operators $a^+, a([a, a^+]_- = 1)$; in so doing for the operators of voltage and current we obtain the expressions: $\hat{V}_T = i\sqrt{\omega_T/2C_T}(a^+ - a), \hat{I}_T = \sqrt{\omega_T/2L_T}(a^+ + a)$. A linewidth broadening γ_T and a finite quality factor of the tank, $Q_T = \omega_T/(2\gamma_T)$, are caused by the tank's own heat bath, which is characterized by the variable Q_b and the Hamiltonian H_{TB}.

Following to Ref.15 we derive the equation for the averaged voltage in the tank coupled to the double dot:

$$\left(\frac{d^2}{dt^2} + \gamma_T\frac{d}{dt} + \omega_T^2\right)\langle\hat{V}_T\rangle = \lambda\frac{\omega_T^2}{C_T}\langle\sigma_z\rangle + \frac{1}{C_T}\dot{I}_{bias}. \tag{3}$$

The particle's variable $\langle\sigma_z\rangle$ is functionally-dependent on the tank's voltage:

$$\langle\sigma_z(t)\rangle = \lambda \int dt_1 \langle \frac{\delta\sigma_z(t)}{\delta f(t_1)} \rangle \langle V_T(t_1)\rangle, \tag{4}$$

where the functional derivative corresponds to the electric susceptibility $\chi_z(\omega)$ of the particle in the double-dot system

$$\langle \frac{\delta\sigma_z(t)}{\delta f(t_1)} \rangle = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t_1)} \chi_z(\omega). \tag{5}$$

The bias current, $I_{bias}(t) = I_{ac}\cos\omega t$, applied to the tank, induces oscillations of the tank's voltage, $\langle V_T(t)\rangle = V_T\cos(\omega t + \Theta)$, with the amplitude V_T and the phase Θ which obey the equation

$$\left[-\omega^2 - i\gamma_T\omega + \omega_T^2 - \frac{\lambda^2\omega_T^2}{C_T}\chi_z(\omega)\right] V_T e^{-i\Theta} = -\frac{i\omega}{C_T} I_{ac}. \tag{6}$$

For the case when the frequency of the bias current is exactly equal to the initial resonant frequency of the tank, $\omega = \omega_T$, the current-voltage phase shift is given by the equation

$$\tan\Theta = -2\lambda^2 \frac{\bar{Q}_T}{C_T} \chi_z'(\omega_T), \tag{7}$$

where $\bar{Q}_T = \omega_T/(2\bar{\gamma}_T)$ is an effective quality factor of the tank, modified because of the double dot contribution to the broadening of the tank's linewidth: $\bar{\gamma}_T = \gamma_T + (\lambda^2\omega_T/C_T)\chi_z''(\omega_T)$.

The electric susceptibility of the double dot, $\chi_z(\omega)$, can be found in the framework of the theory of open quantum systems[15,16]. Quantum dynamics of the charged particle in two-well potential is governed by the Heisenberg equations:

$$\begin{aligned} \dot{\sigma}_x &= -\varepsilon\sigma_y + 2(Q+f)\sigma_y, \\ \dot{\sigma}_y &= -\Delta\sigma_z + \varepsilon\sigma_x - 2(Q+f)\sigma_x, \\ \dot{\sigma}_z &= \Delta\sigma_y. \end{aligned} \tag{8}$$

Here $Q = Q_0 + \lambda\tilde{V}_T$ is the operator of the total dissipative environment which surrounds the double dot. For the susceptibility of this environment we have the relation: $\chi(\omega) = \chi_0(\omega) + \chi_T(\omega)$, where $\chi_0(\omega)$ corresponds to the internal mechanisms of dissipation in the double dot, and

$$\chi_T(\omega) = \frac{e^2}{C_T}\left(\frac{z_0}{d}\right)^2 \frac{\omega_T^2}{\omega_T^2 - \omega^2 - i\omega\gamma_T} \tag{9}$$

describes dissipative properties of the tank which are due to its coupling to the bath Q_b. The spectral functions of the heat bath fluctuations, $S(\omega) = S_0(\omega) + S_T(\omega)$, is related to the imaginary part of the heat bath susceptibility by the fluctuation-dissipation theorem: $S(\omega) = \chi''(\omega)\coth(\omega/2T)$, with T being a temperature of the bath. Averaging the Heisenberg equations (8) over the equilibrium fluctuations of environment followed by an application of Bloch-Redfield approximation allows us to find the electric susceptibility of the charged particle confined in the two-well potential

$$\chi_z(\omega) = -2\Delta \frac{-i\omega + S(\omega+\omega_0) + S(\omega-\omega_0)}{(-i\omega+\gamma_0)[-i(\omega-\omega_0)+\gamma][-i(\omega+\omega_0)+\gamma]} \sigma_x^0. \tag{10}$$

Here $\omega_0 = \sqrt{\Delta^2+\varepsilon^2}$ is the ground-state splitting for the tunneling particle, $\sigma_x^0 = -(\Delta/\omega_0)\tanh(\omega_0/2T)$ is a steady-state value of the matrix σ_x. Coupling of the double dot to the dissipative environment results in the frequency-dependent decoherence and relaxation rates γ and γ_0

$$\begin{aligned} \gamma(\omega) &= \frac{\Delta^2}{\omega_0^2} S(\omega) + \frac{\varepsilon^2}{\omega_0^2}\left(1 - \frac{\omega_0}{\omega}\right) S(\omega+\omega_0) + \frac{\varepsilon^2}{\omega_0^2}\left(1 + \frac{\omega_0}{\omega}\right) S(\omega-\omega_0), \\ \gamma_0(\omega) &= \frac{\Delta^2}{\omega_0^2}\left[S(\omega+\omega_0) + S(\omega-\omega_0)\right]. \end{aligned} \tag{11}$$

In particular, a back-action of the tank on the tunneling particle leads to the small decoherence and relaxation rates

$$\gamma(\omega_0) = \frac{1}{2}\gamma_0(0) = \left(\frac{\Delta}{\omega_0}\right)^2 S_T(\omega_0) = \frac{e^2}{2Q_T C_T}\left(\frac{z_0}{d}\right)^2 \left(\frac{\Delta}{\omega_0}\right)^2 \left(\frac{\omega_T}{\omega_0}\right)^3. \tag{12}$$

It should be emphasized that the current-voltage angle Θ (7) is proportional to the double-dot susceptibility, $\chi_z'(\omega_T)$, taken at the resonant frequency of the tank ω_T, which is much lower than the tunneling frequency ω_0. Taking this fact into account we find the real part of the electric susceptibility: $\chi_z'(\omega_T) = -2\Delta\sigma_x^0/\omega_0^2$. As a result, the phase angle between the voltage in the tank and the bias current is determined by the following equation

$$\tan\Theta = -\frac{e^2}{C_T}\left(\frac{2z_0}{d}\right)^2 Q_T \frac{\Delta^2}{(\Delta^2+\varepsilon^2)^{3/2}} \tanh\left(\frac{\sqrt{\Delta^2+\varepsilon^2}}{2T}\right). \tag{13}$$

By way of illustration, we consider tunneling in an ammonia molecule NH_3 which is described by the two-well potential energy[17]. The existence of two delocalized states with eigenenergies separated by a tunneling splitting $\Delta/h = 23.8$ GHz has motivated to harness this molecule as a quantum bit[9]. According to this proposal the NH_3-molecule can be encapsulated into a fullerene C_{60} to be addressed individually. A direct chemisorption of the ammonia molecule on the surface of a semiconductor represents another possiblity[18]. The fullerene ball incorporating the single ammonia molecule is inserted between the capacitor's plates having an area about 1 μm^2. If the distance between plates is of order of a diameter of $C_{60}-$molecule[19]: $d = 1.2\times 10^{-9} m$, then for the capacitance C_T we get an estimation: $C_T \simeq 10$ fF. Together with a value for the tank's inductance, $L_T \simeq 1\ \mu H$, it gives the resonant frequency of the tank: $\omega_T/2\pi = 1.6$ GHz which is much less than the tunneling frequency $\Delta/h : \hbar\omega_T/\Delta = 0.06$. The electric dipole moment of the ammonia molecule[18], $2ez_0$, which is involved in the formula (13), is of order of $0.31\ e\times 10^{-10}$ m . For the case when losses in the tank are mainly due to a shunt resistance R_T, which is parallel to the capacitor C_T, the linewidth of the tank is defined as: $\gamma_T = 1/(R_T C_T)$, so that the quality factor is $Q_T = \omega_T R_T C_T/2$, and the current-voltage angle Θ does not depend on the capacitance of the tank C_T :

$$\tan\Theta = -\frac{\hbar\omega_T}{2\Delta}\frac{R_T}{(\hbar/e^2)}\left(\frac{2z_0}{d}\right)^2 \frac{\Delta^3}{(\Delta^2+\varepsilon^2)^{3/2}} \tanh\left(\frac{\sqrt{\Delta^2+\varepsilon^2}}{2T}\right). \tag{14}$$

The current-voltage angle Θ can be measured in the experiment as a function of the bias ε applied to the tunneling particle. With a reasonable estimation for the shunt resistance[19]: $R_T = 50\times 10^6$ Ohm, the single ammonia molecule demonstrates a pronounced low-frequency response: $\tan\Theta = -0.23$, at temperatures $T < \Delta/k_B = 1.1$ K, and $\varepsilon = 0$. Measurement-induced decoherence, $\gamma = \gamma(\Delta)$ (12), is negligibly small in the process: $\gamma/\Delta \simeq 10^{-11}$, that allows us to characterize the IMT procedure as a weak continuous measurement[20,21]. To be realistic, for the example under discussion - the ammonia molecule confined inside of C_{60} - we have to take into account screening effects due to a fullerene cage[9]. Because of the screening, a magnitude of the IMT dip (13,14) decreases that can be compensated by a proper increasing of the shunt resistance R_T and the quality factor of the tank Q_T.

In conclusion, we have proposed to use the impedance measurement technique for continuous monitoring of quantum tunneling in molecular systems which are characterized by a two-well potential energy. To this end, the molecule(s) should be inserted between the plates of a capacitor C_T comprising a high-quality superconducting tank along with an inductance L_T. We have shown that the present approach is sensitive enough to detect a tunneling motion in a single molecule.

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